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GB 1546874 A

GB 1500730 A

GB 1377978 A

GB 0935955 A

GB 0534826 A

WO 88/02382 A

WO 84/02915 A

US 3948842 A

JP 63308076 A

JP 59120666 A

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(54) Marine antifouling paint

(57) A water-erodible film-forming polymer contains ester groups hydrolysable in sea water to form free acid or salt groups bound to the polymer. The hydrolysable ester groups are selected from phosphate, phosphonate and phosphinate groups and thio- and amido- derivatives thereof. The polymer is used in coatings which inhibit the adhesion of marine organisms. A typical polymer contains groups derived from methacryloxyethyl diphenyl phosphate.

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This invention is concerned with anti-fouling marine paints used on surfaces likely to come into contact with aquatic fouling organisms such as algae, seaweed and barnacles, for example on ships or boats, or on the out-falls for cooling water from power stations. More particularly, it is concerned with improvements in binders for such paints.

The most successful anti-fouling paints in recent years have been self-polishing anti-fouling paints which use as binders linear polymers containing pendent side groups which are liberated from the polymer on reaction with sea water, the residual polymer being sufficiently dispersible or soluble in sea water to be swept away from the paint surface, exposing a fresh layer of the binder able to undergo a similar reaction with sea water. Such paints are described for example in British Patent 1457590. The gradual thinning of the paint film controls the release of a biocide active against fouling and present either as a pigment in the paint or as a leaving group. The well-known benefits of such self-polishing paints are that the paint film tends to at least retain its initial smoothness and may even become smoother from the action of relatively moving water and that the biocide contained in the paint tends to be delivered from the surface at a uniform or constant rate.

The only commercially significant self-polishing paints employ binders which are copolymers of a triorganotin ester of an olefinically unsaturated carboxylic acid. The triorganotin provides some of the biocidal action of the paints and the triorganotin ester readily undergoes the hydrolysis on which the self-polishing action is dependent. The biocidal activity can be augmented by other anti-fouling substances dispersed or dissolved in the paint film. There may be advantages in a self-polishing

anti-fouling paint which does not rely on the release of triorganotin groups, both for cost reasons and because the powerful biocidal effects of triorganotin may not be desired. There has been concern about the environmental effect of triorganotin biocides released from yachts in particular.

There have been many proposals for a group which substitutes for the triorganotin in forming an easily hydrolysable ester with a polycarboxylic acid polymer, but a commercial self-polishing paint in which the triorganotin moiety has been replaced is still awaited. International Patent Publication WO 84/02915 suggests a wide range of such groups. European Patent Application 232006 suggests a water-erodible polymer comprising one or more hydrolysable sulphonate or sulphate ester groups which in an aqueous environment will generate by hydrolysis corresponding polymer-bound acid groups.

We have found new binders having a rate of hydrolysis suitable for use in self-polishing anti-fouling paints.

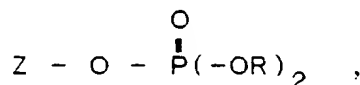
A water-erodible film-forming polymer according to the invention contains ester groups hydrolysable in water, particularly sea water, to form free acid or salt groups bound to the polymer and is characterised in that the hydrolysable ester groups are selected from phosphate, phosphonate and phosphinate groups and thio- and amido-derivatives thereof.

The invention includes a process for coating a marine surface to inhibit the adhesion of marine organisms, characterised in that the surface is coated with a water-erodible film-forming polymer as defined above in accordance with the invention. By a "marine surface" we mean the underwater hull surface of a ship or boat or another surface which is in contact with sea water in use. Other uses for the water-erodible film-forming polymer according

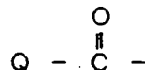
to the invention are in dental hygiene, non-fouling membranes and bioreactor surfaces and medical prostheses.

The invention includes an anti-fouling marine paint comprising a pigment, a biocide for marine organisms and a water-erodible film-forming polymer as defined above in accordance with the invention. The pigment and biocide can be two different components of the paint, or one material having both properties can act both as a pigment and as a biocide.

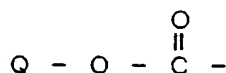
The polymer is preferably a linear polymer but can be branched or crosslinked provided that the hydrolysed polymer is soluble in sea water. The hydrolysable ester groups can be present in the main polymer chain but are preferably present in groups pendent to the main polymer chain. Examples of types of ester groups which can be present in pendent groups include phosphate groups of the formula



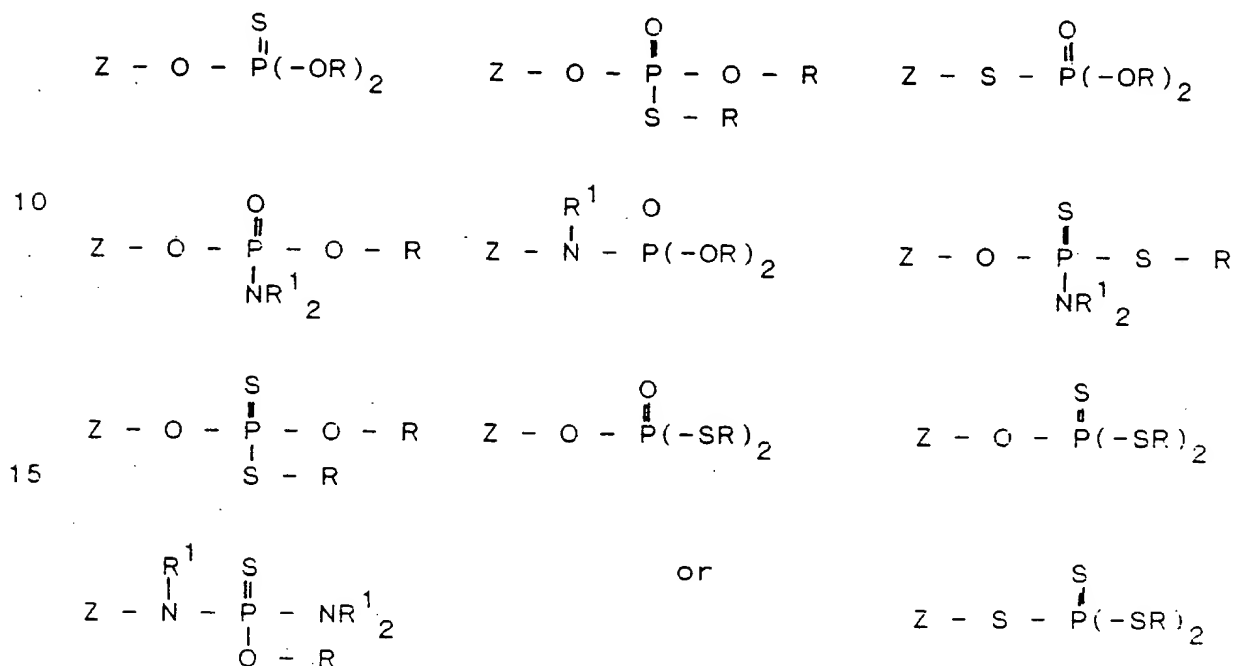
where Z denotes the attachment of the group to a polymer residue and each R is a monovalent organic group. The groups R can for example be selected from alkyl, aryl or aralkyl groups, e.g. of up to 8 carbon atoms, any of which can be substituted, for example by hydroxy, alkoxy, amino, nitro, or halide groups. Alternatively, one or both of the groups R can be acyl of the formula



or carboxyl ester of the formula

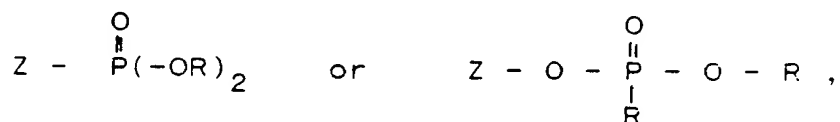


where Q is a monovalent hydrocarbyl group, e.g. of up to 8 carbon atoms, which can be substituted. Thio- and amido-derivatives containing one or more sulphur atoms or -NR¹ groups, where R¹ is hydrogen or a monovalent organic radical, e.g. of up to 8 carbon atoms, replacing oxygen in the phosphate group can also be used, for example



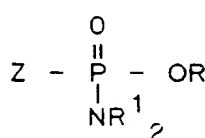
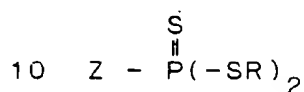
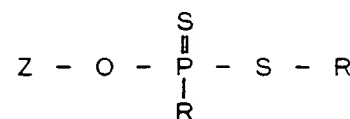
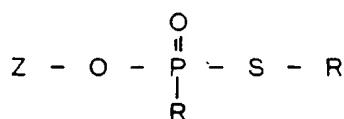
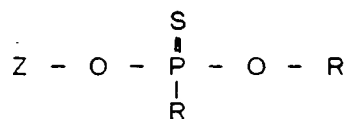
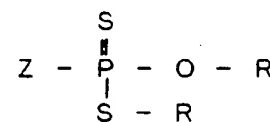
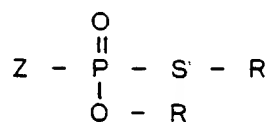
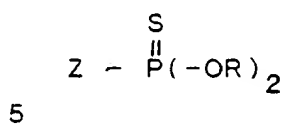
Alternatively, one or both of the groups R can be a further polymer residue; that is the phosphate ester group can be used as a crosslinking group in a polymer. Such a phosphate ester crosslinking group will hydrolyse to leave a water-soluble residue.

Other examples of hydrolysable ester groups are phosphonate groups of the formula



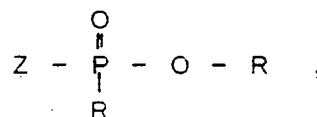
where Z and R are defined as above. Thio- and amido-

derivatives of the phosphonate groups can be used, for example

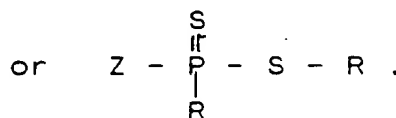
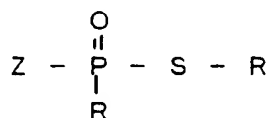
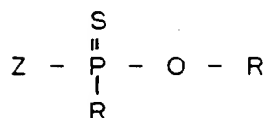


Alternatively, one or both of the groups R can be a polymer residue in a hydrolysable crosslinked polymer.

Examples of hydrolysable ester groups also include
15 phosphinate groups of the formula

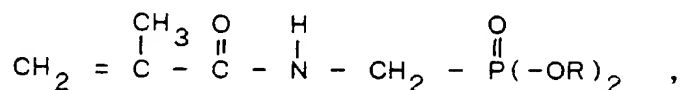


where Z and R are defined as above, and corresponding thio-
20 derivatives of the formulae

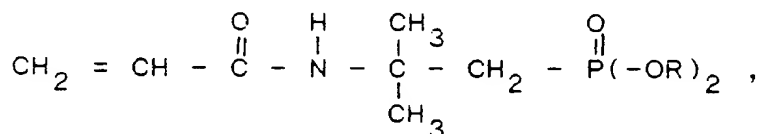


In the case of phosphonate or phosphinate groups it is
25 preferred that the phosphorus atom is bonded directly to a carbon atom of the polymer residue rather than through an oxygen or sulphur atom. Such phosphonates and phosphinates are particularly preferred in the polymers of the invention.

The polymer residue to which the groups are attached is preferably derived from an addition polymer formed by the polymerisation of an unsaturated monomer containing the phosphate, phosphonate or phosphinate ester group. For example, the monomer can be a diester of an acrylamido-alkane or methacrylamido-alkane phosphonic acid such as methacrylamido-methane phosphonic acid, of the formula



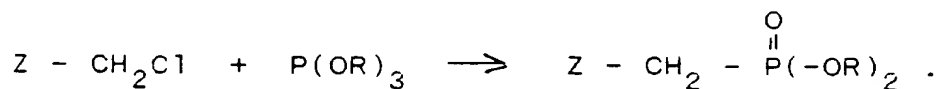
for example the dimethyl, diethyl, methyl phenyl or diphenyl ester, or a diester of 2-acrylamido-2-methylpropane phosphonic acid, of the formula



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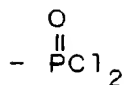
or of 2-acrylamido-ethane phosphonic acid or styrene phosphonic acid.

Alternatively, a polymer containing pendent halo-alkyl groups, for example the polyether having pendent chloromethyl groups sold under the Trade Mark "Hydrin", can be reacted with a phosphite triester to introduce pendent phosphonate groups, as follows



A phosphite diester salt such as $(\text{RO})_2\text{PO}^-\text{Na}^+$ can be used in place of the phosphite triester.

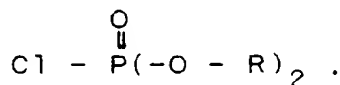
Treatment of a polyolefin such as polyethylene with PCl_3 in the presence of oxygen can introduce pendent dichlorophosphonate groups of the formula



bonded to the polymer chain, and these dichlorophosphonate groups can then be reacted with an alcohol ROH to form
5 phosphonate ester groups.

In one preferred method for forming polymers containing phosphate ester groups, a polymer containing hydroxyl groups is reacted with a phosphate diester monoacid chloride

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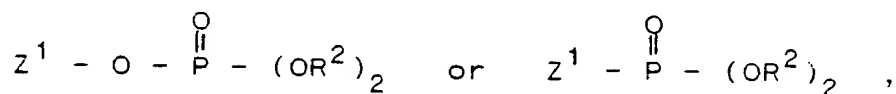


The reaction can be carried out in an organic solvent in the presence of a base such as triethylamine or pyridine. Examples of suitable polymers containing hydroxyl groups
15 are polymers of hydroxyalkyl acrylates or methacrylates such as hydroxyethyl methacrylate, hydroxyethyl acrylate or hydroxypropyl methacrylate. Alternatively, a hydroxyalkyl acrylate or methacrylate monomer can be reacted with the acid chloride and subsequently polymerised. Examples of
20 solvents which can be used for the reaction are ketones such as methyl isobutyl ketone or mixtures thereof with an aromatic hydrocarbon such as xylene.

An alternative hydroxy-functional polymer which can be reacted with a phosphate diester monoacid chloride is a
25 hydroxy-functional polyester or polyether. Hydroxy-functional polyesters can be produced by the reaction of a dicarboxylic acid or an anhydride thereof, for example terephthalic, isophthalic, adipic or sebacic acid and/or phthalic anhydride, with an excess of a diol such as
30 ethylene glycol, propylene glycol, butane-1,4-diol, neopentyl glycol and/or an ether glycol such as diethylene glycol, triethylene glycol or dipropylene glycol. The polyester can be a block copolymer containing polyether

blocks derived from polyethylene glycol or poly(tetramethylene ether) glycol. A suitable hydroxy-functional polyether can for example be formed by reaction of an amine-tipped polyether with an epoxide to form
 5 bis(beta-hydroxy) amine groups.

Not all phosphate and phosphonate ester groups are readily hydrolysable in sea water. Normal trialkyl phosphates and dialkyl alkylphosphonates, for example, are not substantially hydrolysable in sea water. The corresponding polymers containing groups of the formula
 10



where Z^1 denotes the attachment of the group to a chain of 2 or more aliphatic carbon atoms on a polymer residue and
 15 R^2 represents an unsubstituted alkyl group, do not hydrolyse in sea water at a rate sufficient for use in polishing anti-fouling paints.

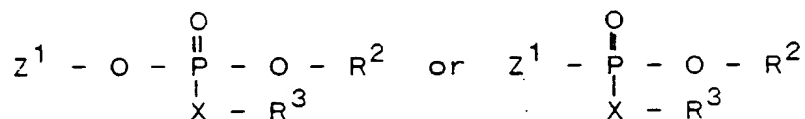
A test procedure for measuring the rate of hydrolysis of polymer films is described in PCT Patent Application
 20 WO84/02915. The hydrolysis of polymer films in pH=9 water at 35°C is measured by back-titrating the polymer-free acid with standardised KOH at 24 hour intervals. Hydrolysis is conducted in a single-neck, 300 ml flask, stirred by a 3/4" (1.9 cm) PTFE-coated magnetic stirrer, immersed in a
 25 thermostatically-controlled water bath at $35 \pm 1^\circ\text{C}$ under an inert atmosphere obtained by bubbling nitrogen below the surface of the resin-water mixture for about one half hour and then sealing the flask. The flask contains 150 ml of distilled water at a pH of 9.0 with KOH and 5.0 g of
 30 vacuum-dried polymer film pulverised in a Waring blender for 20-30 seconds. The pH is measured on a pH Meter using a combination glass/KCl electrode. Every 24 hours the contents of the flask are back-titrated to pH 9.0 with standardised KOH and the number of milliequivalents used is

calculated. Five consecutive 24-hour titrations are carried out. Polymers which show hydrolysis rates above

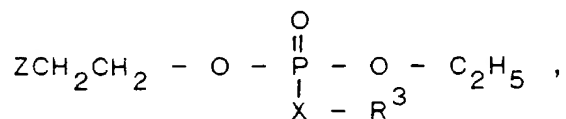
5×10^{-4} meq/hr are preferred for serving as binders for water-insoluble sea-water-erodible anti-fouling paints.

- 5 In one preferred type of phosphate ester or phosphonate ester group, one of the esterifying radicals R is a Leaving Group which is more readily hydrolysed than a normal alkyl group. The water-erodible polymer can thus contain groups of the formula

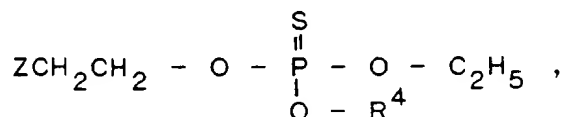
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- where Z^1 and R^2 are defined as above, X is oxygen or sulphur and R^3 is a leaving group. In the case of
15 phosphate ester groups in which R^2 is an alkyl group, for example of the formula

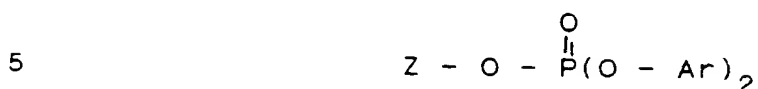


- 20 the group R^3 is preferably such that the corresponding compound $R^3\text{XH}$ has a pKa of less than 9 (at 25°C). Examples of such groups R^3 when X is oxygen are nitrophenyl and p-cyanophenyl, and when X is sulphur R^3 can be p-methylphenyl. In the case of phosphorothionate ester groups of
25 the formula



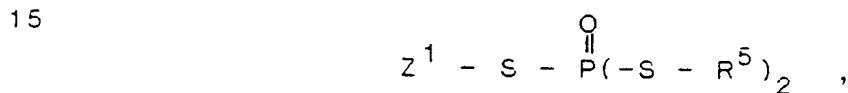
- the required pKa of the compound $R^4\text{OH}$ is less than 6 (at
30 25°C). An example of such a group R^4 is 4-pyrimidinyl.

Aryl phosphates are generally more readily hydrolysable than alkyl phosphates. For example, a polymer containing groups of the formula



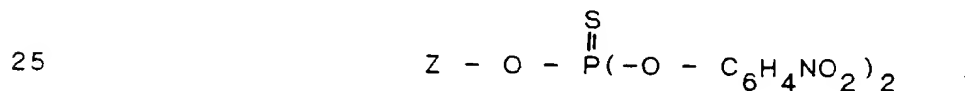
where each Ar is an aryl group, for example a phenyl or nitrophenyl group, is hydrolysed at a sufficient rate in sea water. Examples of polymers containing such groups are 2-methacryloxy-ethyl and 2-acryloxy-ethyl diphenyl phosphate.

Alkylthio groups attached to the phosphorus atom are more readily hydrolysed than alkoxy groups. For example, polymers containing phosphorotrithiolate groups of the formula

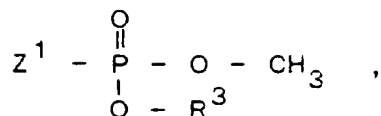


where R^5 is alkyl, are hydrolysed in sea water at a sufficient rate.

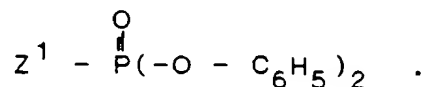
Phosphorothionate groups on the other hand are less readily hydrolysed than phosphate groups and may require two Leaving Groups. An example of a phosphorothionate group which is hydrolysable in sea water at a sufficient rate is



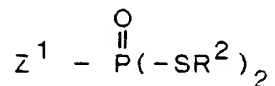
When the polymer contains phosphonate ester groups of the formula



5 R^3 can for example be a nitrophenyl group or any of the groups R^3 suggested above for use in phosphate esters. The phosphonate ester groups can alternatively be diaryl phosphonate groups of the formula

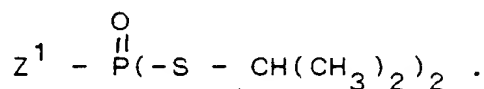


10 Dithiophosphonates of the formula

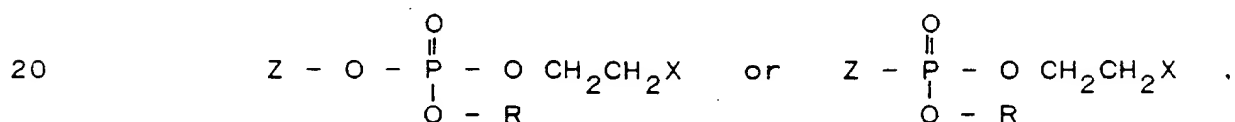


are also hydrolysable in sea water at a sufficient rate, for example groups of the formula

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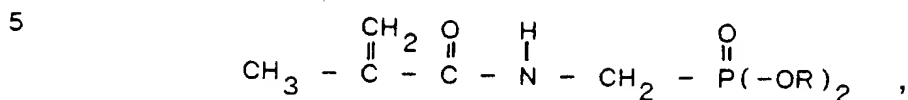
The phosphate or phosphonate ester groups can alternatively be of the form



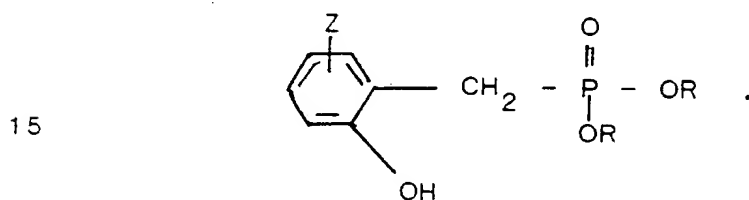
where X is a group which activates beta-elimination in the presence of the hydroxide ion present in sea water, for example an aldehyde, cyano, sulphone such as $-\text{SO}_2\text{CH}_3$ or
25 $-\text{SO}_2\text{CH}_2\text{C}_6\text{H}_5$ or ketone, e.g. $-\text{COCH}_3$, group.

Electron-donating groups proximate to the phosphonate ester groups can have an anchimeric effect, promoting the hydrolysis of the phosphonate ester. With suitable polar

groups in the linkage to the polymer chain, hydrolysis of simple aryl or even alkyl ester groups is possible. In polymers of methacrylamido-methyl phosphonate esters containing the group



the amide group promotes the hydrolysis of the phosphonate ester linkages. Alternatively polymers having one or two electron-withdrawing groups such as chlorine on the carbon adjacent to the phosphonate group are readily hydrolysed. Another type of activating group is a substituted aryl group, for example of the form

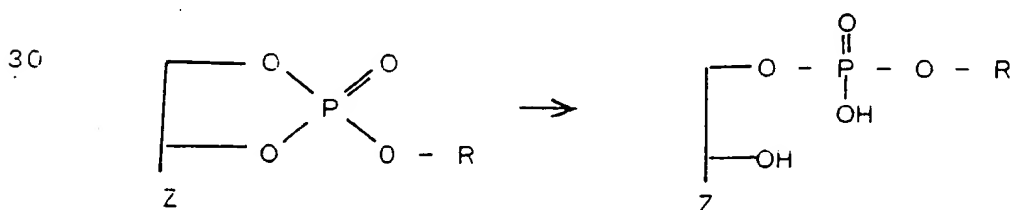


Phosphinate ester groups are more readily hydrolysable in sea water than phosphonate or phosphate groups. For example, a group of the formula

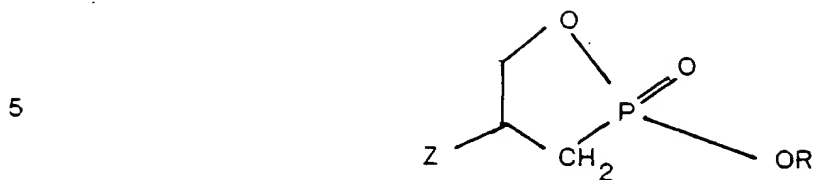


will hydrolyse at a sufficient rate.

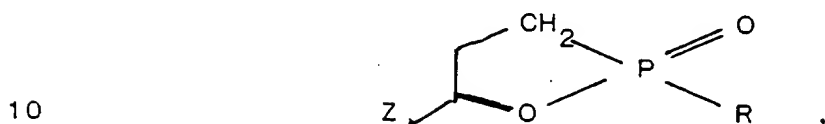
Another type of preferred phosphate ester group is a cyclic phosphate ester, which can be hydrolysed to generate an acid phosphate group and a hydroxyl group, both attached to the polymer. An example of such a hydrolysable cyclic ester group is



Cyclic phosphonate and phosphinate ester groups, for example of the formula

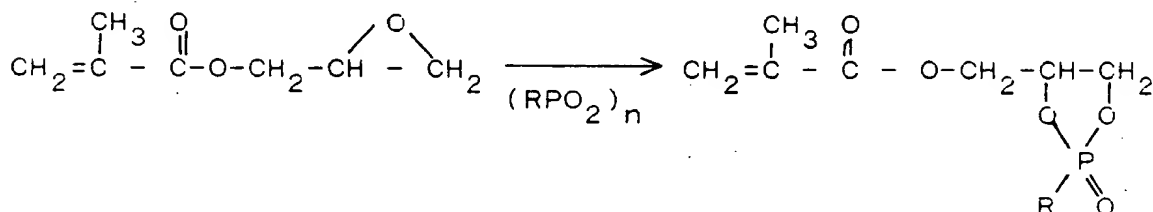


or



are also preferred.

In one method of forming cyclic phosphate or phosphonate ester groups glycidyl acrylate or monomethacrylate can be reacted with a phosphate acid anhydride or phosphonic acid anhydride.



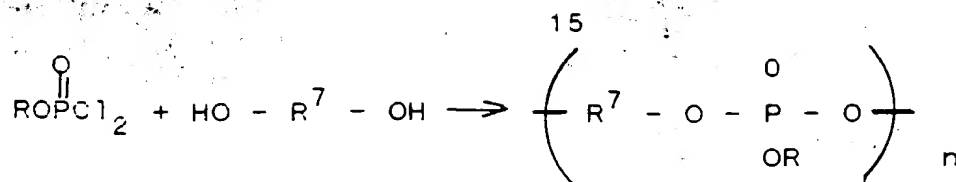
Such cyclic esters can be polymerised by addition polymerisation and are readily hydrolysable in sea water.

The addition polymer can be a homopolymer but is preferably a copolymer containing at least 3 mole % of units of the monomer having hydrolysable phosphate, phosphonate or phosphinate ester groups, together with units of an olefinically unsaturated comonomer. Most preferably the copolymer contains 5-30 mole %, especially 10-25 mole %, of the hydrolysable ester groups. Examples of comonomers which can be used are acrylic monomers such

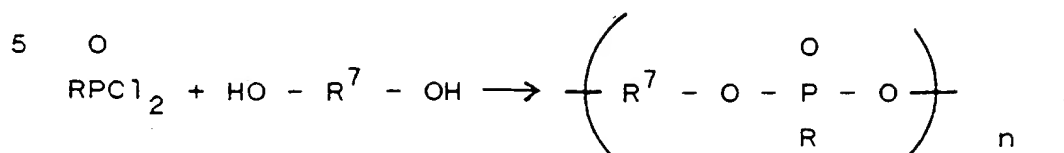
as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, methyl methacrylate and the other corresponding esters of methacrylic acid, acrylonitrile and methacrylonitrile, and vinyl monomers such as vinyl acetate, vinyl butyrate, vinyl chloride, vinyl propionate, styrene and vinyl pyridine. The polymer can also contain monomer units conferring increased hydrophilicity, for example up to 20 mole % of maleic or itaconic anhydride, acrylamide, methacrylamide or N-vinyl pyrrolidone. Some phosphate ester monomers may give rise to a rather soft polymer but this can be counteracted by using a high proportion of a comonomer which tends to form hard polymers, for example methyl methacrylate or styrene. Methyl methacrylate is the most preferred comonomer. The presence of a high proportion of styrene units in the polymer may tend to retard the dissolution of the polymer in sea water, so that a high proportion of hydrolysable ester monomer within the preferred range is generally used in a copolymer with styrene.

The film-forming polymers described above can be prepared by addition polymerisation of the monomers in the appropriate proportions at polymerisation conditions using a free radical catalyst such as benzoyl peroxide or azobisisobutyronitrile in an organic solvent such as xylene, toluene, butyl acetate, butanol, 2-ethoxy-ethanol, cyclohexanone, methyl ethyl ketone, methyl isobutyl ketone, 2-methoxy-ethanol, 2-butoxy-ethanol and/or 2-ethoxy-ethyl acetate. Polymerisation is preferably carried out at a temperature in the range 50 to 150°C.

Alternatively, the hydrolysable phosphate, phosphonate or phosphinate groups can be present in the polymer chain. For example a phosphate acid chloride or phosphonic acid chloride can be heated with a diol to form a polymer according to the reaction.



or



where R^7 is a divalent organic group. The diol $\text{HO} - \text{R}^7 - \text{OH}$ can for example be ethylene glycol, propylene glycol, 1,4-butanediol, neopentylglycol, cyclohexanedimethanol or bisphenol A.

Methods of forming phosphorus-containing polymers are described generally in J. Macromol. Sci. (Revs) C1(i): 1 (1967) by M. Sander and E. Steininger, and these methods can be used to prepare the polymers of the invention.

The acid phosphate or phosphonic or phosphinic acid groups generated by hydrolysis may themselves inhibit the adhesion of marine organisms by forming a highly charged surface at the polymer/sea water interface and as such may be suitable for use as a non-fouling paint without any marine biocide. In any case they render the polymer water-erodible, that is capable of being gradually dissolved away from the paint surface on a ship's hull in service. The polymer can thus be used as the binder of a self-polishing anti-fouling paint.

To form the paint, the hydrolysable polymer binder is mixed with the pigment or pigments used in the paint and with the marine biocide if this is different from the pigment(s). Conventional blending procedures can be used. The pigment generally has a solubility in sea water of below 10 parts per million by weight and is preferably a sparingly soluble pigment having a solubility in sea water

of from 0.5 to 10 parts per million, for example cuprous oxide, cuprous thiocyanate, zinc oxide, zinc chromate, zinc ethylene bis(dithiocarbamate), zinc dimethyl dithiocarbamate or zinc diethyl dithiocarbamate. These sparingly soluble copper and zinc compounds are generally marine biocides. These sparingly soluble pigments produce water-soluble metal compounds on reaction with sea water so that the pigment particles do not survive at the paint surface; this aids the smooth dissolution of the paint in relatively moving sea water. Mixtures of sparingly soluble pigments can be used, for example cuprous oxide, cuprous thiocyanate or zinc ethylene bis(dithio carbamate) which are the most effective biocidal pigments can be mixed with zinc oxide which dissolves slightly more rapidly in sea water and is more effective at inducing the smooth dissolution of the paint.

The paint composition can additionally or alternatively contain a pigment which is not reactive with sea water and may be highly insoluble in sea water (solubility below 0.5 ppm by weight) such as titanium dioxide or ferric oxide. Such highly insoluble pigments are preferably used in proportions up to 40 per cent by weight of the total pigment component of the paint, most preferably less than 20 per cent by weight.

The proportion of pigment to polymer binder is preferably such as to give a pigment volume concentration which is above 25 per cent in the dry paint film but below the critical pigment volume concentration; most preferably the pigment volume concentration is from 35-50 per cent.

The biocidal effect of the sparingly sea water-soluble pigments, particularly cuprous oxide, cuprous thiocyanate and zinc ethylene bis(dithiocarbamate), may be sufficient so that the paint needs no further biocide.

For encountering severe fouling the paint may contain

an added biocide. Triorganotin salts and oxides such as triphenyltin fluoride, tributyltin fluoride, tributyltin dibromosuccinate, triphenyltin chloride, triphenyltin hydroxide and tributyltin oxide are effective marine biocides and can be used in paints according to the invention. A paint according to the invention comprising a triorganotin salt (up to 25 per cent by volume of the pigments) may have anti-fouling and smoothing properties equal to a triorganotin copolymer paint of much higher triorganotin content. In most cases it will be desired to avoid completely the release of triorganotin ions. Examples of other biocides effective as marine anti-fouling agents are dithiocarbamate derivatives such as cupric ethylene bis(dithiocarbamate) or tetramethyl thiuram disulphide, methylene bis(thiourea), 4-butyl catechol, captan, tetrachloroisophthalonitrile, 1-methylthio-3-(t-butylamino)-5-(cyclopropylamino)-s-triazine, or a halogenated isothiazolone such as 4,5-dichloro-2-octyl-3-isothiazolone.

The invention is illustrated by the following Examples.

Example 1

a) Preparation of methacryloxyethyl diphenyl phosphate

A solution of 80.6g diphenyl chlorophosphate $\text{ClP(O)(OC}_6\text{H}_5)_2$ in 150ml CH_2Cl_2 was added dropwise to a cooled solution of 39.0g hydroxyethyl methacrylate and 30.4g triethylamine in CH_2Cl_2 at 0°C . The mixture was left at room temperature for 24 hours. The triethylamine hydrochloride precipitate was removed by filtration and the filtrate was rotary-evaporated to reduce the volume of CH_2Cl_2 . The resulting solution was extracted with 0.1M HCl (2 x 20ml), neutralised with NaHCO_3 solution, then washed with water (4 x 20ml). The organic layer was dried over MgSO_4 overnight. The product was obtained by rotary

evaporation of the dried organic layer to remove the CH_2Cl_2 .

b) Homopolymerisation of methacryloxyethyl diphenyl phosphate

5 20g methacryloxyethyl diphenyl phosphate and 0.02g azobisisobutyronitrile were dissolved in 20ml methyl ethyl ketone (MEK) in an addition funnel. 17ml MEK was heated to 80°C in a flask. The monomer solution was added to the flask over 30 minutes and heated at 80°C for a further 3
10 hours. A clear viscous polymer solution was formed.

The polymer was precipitated from petroleum spirits (boiling point 60-80°C). A portion was re-dissolved in CH_2Cl_2 , cast as a film on a polytetrafluoroethylene sheet and vacuum-dried at 40°C. The resulting polymer film was
15 flexible and transparent.

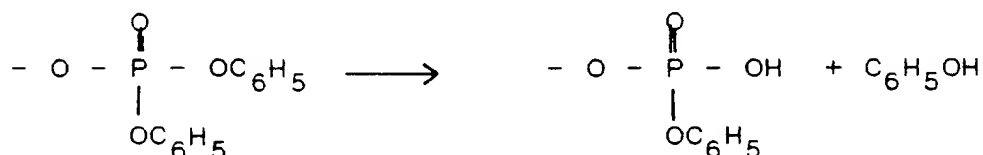
Examples 2 and 3

Following the procedure of Example 1(b), copolymers were prepared using the following solutions, using a proportional amount of MEK heated in the flask initially.

20	Example 2	Example 3
Methacryloxyethyl diphenyl phosphate	25g	20g
Methyl methacrylate	38.2g	15.3g
Butyl acrylate	-	19.5g
25 Azobisisobutyronitrile	0.063g	0.055g
MEK	50ml	38ml

In both cases a clear viscous polymer solution was formed from which a polymer could be recovered and cast as a film, as described in Example 1(b). Polymer solutions (40% solids) in MEK were prepared of each of the polymers of Examples 1 to 3. They were applied as coatings of 100 microns dry film thickness to glass slides using a cube applicator. The coatings were allowed to dry in air for 2 days prior to study, then immersed in static sea water in the laboratory.

The expected hydrolysis of the phosphate ester groups is



A U.V. study was set up to detect phenol in the sea water. To avoid any residual monomer leached from the coating interfering with the phenol signal, the coatings were immersed in sea water for 2 weeks prior to carrying out the U.V. study, the water being changed every day to remove the residual monomer effectively. After the 2-week period, fresh sea water was added and U.V. spectra of the sea water were recorded after given time periods.

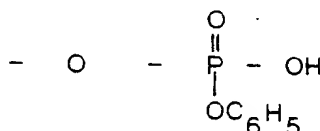
Phenol shows 2 absorptions in sea water, at 204nm (strong) and 264nm (weak). Unfortunately, sea water absorbs strongly between 200-225nm, so that only the intensity of the 264nm absorption can be used for quantitative studies. The sea water samples from all three coatings showed peaks at 204nm and some absorption at 264nm. The sample in contact with the coating of Example 1 clearly showed the peak at 264nm and the peak height increased with time of immersion as follows.

Immersion period E max(264nm)

	9 days	.0227
	21 days	.0519
	30 days	.0729
5	44 days	.0956

These results show that sustained hydrolysis of the phosphate ester groups is occurring. Using NMR and infrared spectroscopy, it was not possible to determine the presence of

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groups in the coating film. This indicates that the hydrolysis occurring is surface hydrolysis with gradual
15 dissolution of the hydrolysed polymer.

Example 4

96.6g methyl methacrylate, 123.7g n-butyl acrylate
126.6g methacryloxyethyl diphenyl phosphate and 3.08g
azobisisobutyronitrile were dissolved in 76g xylene under
20 nitrogen and added over 90 minutes to 280g xylene preheated
to 80°C while purging with nitrogen. Heating was con-
tinued for a further 4 hours. A clear, pale yellow, 47.4%
solids, polymer solution, of viscosity 3.2 poise, was
obtained.

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Example 5

155.0g methacryloxyethyl diphenyl phosphate, 69.0g
methyl methacrylate and 2.51g azobisisobutyronitrile were
dissolved in 63g xylene and added over 3 hours to a solu-
tion of 88.4g butyl acrylate in 252g xylene preheated to
30 80°C. Heating was continued at 80°C for 2 hours and at

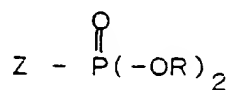
90°C for an hour. A hazy polymer solution was produced, which could be cleared by dilution with methyl isobutyl ketone or butyl acetate to 40% solids.

The polymer solutions of any of Examples 1 to 5 could be used as the binder for an antifouling paint containing cuprous oxide as biocidal pigment.

Claims

1. A water-erodible film-forming polymer containing ester groups hydrolysable in sea water to form free acid or salt groups bound to the polymer, characterised in that the hydrolysable ester groups are selected from phosphate, phosphonate and phosphinate groups and thio- and amido-derivatives thereof.

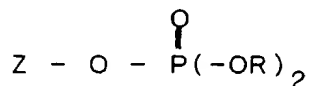
2. A polymer according to claim 1, characterised in that it contains as hydrolysable ester groups phosphonate groups of the formula



where Z denotes the attachment of the group to a polymer residue and each group R is independently selected from alkyl, aryl and aralkyl groups, any of which can be substituted.

3. A polymer according to claim 2, characterised in that the polymer contains units of a diester of an acrylamido-alkane or methacrylamido-alkane phosphonic acid.

4. A polymer according to claim 1, characterised in that it contains as hydrolysable ester groups phosphate groups of the formula

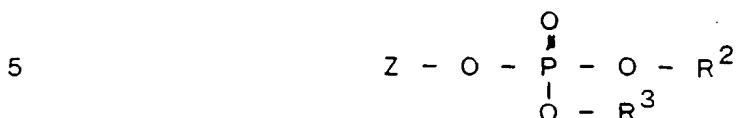


in which Z and R are as defined in claim 2.

5. A polymer according to claim 4, characterised in that the polymer contains units of an acryloxy-alkyl or methacryloxy-alkyl phosphate ester.

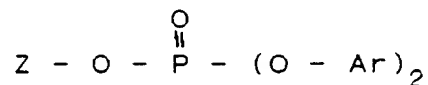
methacryloxy-alkyl phosphate ester.

6. A polymer according to claim 4 or 5, characterised in that the polymer contains units of the formula



where Z is defined in claim 2, R^2 represents an alkyl group and R^3 represents a group such that the corresponding hydroxy compound R^3OH has a pK_a of less than 9 at 25°C .

10 7. A polymer according to claim 4 or 5, characterised in that the polymer contains groups of the formula

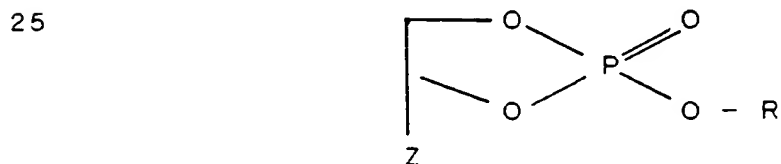


15 where Z as defined in claim 2 and each Ar independently is an aryl group.

8. A polymer according to claim 7, characterised in that both groups Ar are phenyl groups.

9. A polymer according to claim 8, characterised in that the polymer contains units of methacryloxy-ethyl or
20 acryloxy-ethyl diphenyl phosphate.

10. A polymer according to claim 1 characterised in that it contains as hydrolysable ester groups cyclic phosphate ester groups of the formula



where Z and R are as defined in claim 2.

11. A polymer according to any of claims 1 to 10, characterised in that the polymer is a addition copolymer containing 5 to 30 mole per cent of polymerised units of a monomer having a hydrolysable phosphate, phosphonate or phosphinate ester group or thio or amide derivative thereof, the balance being polymerised units of one or more comonomers.

12. A water-erodible film-forming polymer as claimed in claim 1 and substantially as hereinbefore described.

10 13. A process for coating a marine surface to inhibit the adhesion of marine organisms, characterised in that the surface is coated with a water-erodible film-forming polymer according to any of claims 1 to 12.

15 14. An anti-fouling marine paint comprising a pigment which is a biocide for marine organisms, or a pigment and a separate biocide for marine organisms, and a water-erodible film-forming polymer according to any of claims 1 to 12.